Effects of Organic Acids on Heavy Metals Release From Mine Tailings

Ashley H. Munyai, Elvis Fosso-Kankeu and Frans Waanders

Abstract**—**The batch leaching experiment was conducted in order to mobilize metals from mine tailings by using organic acids. Characterization of tailings samples were conducted using X-Ray diffraction (XRD) and X-Ray fluorescence (XRF). The results have indicated that sillimanate and Iron catena-sillimanate were the major mineralogical composites while Ca and Fe were the major metals in the mine tailings. Five organic acids namely malic, gluconic, oxalic, and citric acids were used as leaching agents. The effect of time, pH and temperature were examined in this study. The results obtained have revealed that Fe and Ca are leached out in high concentration at low pH (more acidic) and at high temperature. Metal affinity among organic acids was found to vary as oxalic and citric acids exhibited better leaching performance than the others.

Index Terms**—** Mine tailings, Organic acid, metal mobility, Temperature, pH, time

I. INTRODUCTION

Tailing wastes from mining activities consist of different toxic elements which results after extraction of minerals, thus cause pollution of the environment [1]. The weathering of tailings can cause the deposition of heavy metals associated with sulphide minerals to the soil and hydrological systems around the mine [2]. In general mine soils are mechanically, physically, chemically and biologically deficient [3], characterized by instability and limited cohesion, with low contents of nutrients and organic matter and high levels of heavy metals [3]. When mine wastes are exposed to the atmosphere and water frequently, it causes the oxidation of ore-associated sulphides such as pyrite (FeS_2) and pyrrotite ($Fe_{1-x}S$), accompanied by the formation of (AMD) [4]. The mobility of heavy metals from wastes in aqueous system is the worrying factor, because of the intrinsic solubility at varying pH, reduction-oxidation characteristics and complex forms tendencies [5]. Microorganisms in tailings fed on organic matter for growth and energy which may cause it to contribute in leaching of metals [6]. During the degradation of the organic matter, heterotrophic organisms release variety of low molecular weight organic acids, which mobilize the metals [7]. The role of microbes in nature has been well documented particularly for weathering of metal containing rocks, minerals, metals and coals [5], leading to the mobilization, dissociation of metal ions, formation of acid mine drainage (AMD) through oxidation-reduction, and times precipitation/ transformation of metals to a different state such as oxides, hydroxide, sulphide etc. Microorganisms are nowadays preferred in industries for removal and recovery of metals, as the process is environmental friendly and inexpensive than the chemical methods and conventional methods [8]. Such microorganisms utilize the organic acids they metabolize to remove metals from it wastes. Predicting the release of metals in different environmental condition could help acquaint people in South Africa about the danger mine tailings possess. Many studies regarding the release of metals by using organic acids have been done, but were not conducted in South Africa. In the present study, the influence of organic acids under different environmental conditions was investigated.

II. METHODOLOGY

A. Materials

Mine tailings used were collected from an abounded mine located in the Krugersdorp area, South Africa. The tailings samples were taken from the top 30 cm of the surface at 2 locations using an auger drill. For this study tailing samples used were the representative from the top of the tailing dump (S2) and from the bottom of the tailing dump (S13). All samples were air dried at 80°C for 2 days, crushed by hand using porcelain mortar, sieved through 75 µm to a powder form. The powder form samples were used in the entire batch leaching experiment, the remaining of samples were kept in plastics bags prior to use in the rest of experiment.

B. Characterization of mine tailings by XRD and XRF

The mineralogical study of the tailings samples were carried out by means of X-ray diffraction (XRD) analysis. The bulk composition was determined using the powder diffraction method, after grinding and homogenization of the samples to 75 µm particle sizes. Nonoriented powders were examined on a Philips X'pert MPD diffractometer, at a power of 1.6 kW operating at 40 KV. Major and trace elements of the tailings were analysed using the X-ray- fluorescence spectrometer (XRF) which was done on the magiX PRO SuperQ Version 4. A rhodium (Rh) anode was utilized in the X-ray tube and operated at 50 kV and current 125 mA; at power level of 4 kW.

C. Batch leaching

Batch experiments were conducted to determine the effect of organic acids (malic, gluconic, oxalic, and citric acids) on the mobilization of metals, such as Fe and Mg from contaminated tailing at various concentrations of organic acids (1, 10, and 100 mM) and initial pHs (3.5, 4.5, 5.5, and 6.5) and temperatures (30°C,40°C and 50°C) for all the experiments, one representative sample from the top (S2) and

Elvis Fosso-Kankeu is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa

Frans Waanders is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa

Ashley Munyai is with the School of Chemical and Minerals Engineering of the North West University, Bult area-Potchefstroom-South Africa

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one from the bottom (S13) of the dump, were used. The experiments were conducted as follows:

Effect of time

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (malic, gluconic, oxalic, and citric acid).

The experiment was conducted in duplicate. The mixture added into volumetric flasks was then shaken by hand for 1 minute to ensure full saturation of the tailing with the solution and then shaken on orbital shaker at room temperature, and 200 rpm for 8, 20, 40 and 48 hours.

The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis.

The samples kept in a fridge were then be analysed for heavy metals using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent Technologies, USA).

Effect of pH

A mass of 2.5g of tailing was added to 25 mL of 3 mM organic acid (oxalic, and citric acid) and initial pHs (3.5, 4.5, 5.5, and 6.5).

The experiment was conducted in duplicate. The pH was controlled with HCl and NaOH. The mixture was added in to volumetric flasks then shaken on orbital shaker at room temperature for 24 hrs at 200 rpm. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis. The samples kept in a fridge were then analysed for heavy metals.

The effect of temperature

A mass of 2.5 g of tailing was added to 25 mL of 3 mM organic acid (oxalic and citric acids). The experiment was conducted in duplicate. The mixture was added into conical flasks, then shaken on an orbital shaker at various temperatures (20, 30 and 40 °C). The experiment was conducted at various time for 8 hrs, 20 hrs, 40 hrs and 48 hrs. The pH was measured after shaking and then the samples were centrifuged for 10 minutes at 4000 rpm, then the supernatant was kept in a fridge before analysis.

III. RESULTS AND DISCUSSION

Characterization of mine tailings

XRD

The mineralogical composition of the 2 representative samples used in this study is summarized in Table 1. The mineralogical composition of tailing samples was determined by X-ray diffraction (XRD). The results indicate that sillimate and Iron catena-sillicate were the main mineral composites of the tailing from the Krugersdorp mining area.

TABLE I
MINERALOGICAL COMPOSITION OF MINE

Minerals	Top sample (S2)	Bottom sample (S13)
	Weight%	Weight%
Quartz	0.6	8.2
Fayalite	3.3	
Sillimanate	0.27	8.5
Iron catena-sillicate Ferrosillite	95.83	
Wustite		6.56

XRF

The major, minor and trace elements were determined by using XRF analysis, represented in Table 2. SiO_2 is the dominant oxide in all samples collected from the Krugersdorp mining area. SiO_2 was also found to be major constituent in mine tailings studied by Novhe et al [9, 10]. Elements such as Al, Cr, Ni, Zn, Cu, As, Pb, K, Mg, Na and Co were also identified in the tailings samples, but were not present in all samples. Those which were identified in all samples included elements such as Ca, Cr, Fe, K, Mg, Na, Pb and Zn, however in the present study only Ca and Fe remained as main focus because they were relatively abundant.

TABLE II
MAJOR TRACE ELEMENTS IN TAILINGS

Samples	CaO	Fe2O3	SiO2
	Weight%	Weight%	Weight%
Top sample (S2)	0.0826	2.6767	81.3664
Bottom (S13)	0.1653	0.9971	89.1518

B. batch leaching experiments

Effect of contact time

Figure 1 represents the effect of time on the leaching or mobilization of metals considered in the study using various organic acids such as oxalic, citric, tartaric, malic and gluconic acids. The results have shown a decrease in concentration of Fe for sample from top and bottom of the tailing dump as time increases, which indicate the very high leaching rate/mobility within the initial hours of leaching. High amounts of Fe released from the bottom sample (S13) at 8 hours being 31.13 mg/L, 18.71 mg/L and 16.48 mg/L for leaching agents oxalic, citric, and tartaric acids respectively. Leaching of the sample from the top of the dump (S2) with oxalic acid, citric acid and gluconic acid allowed achieving high leaching rate at 8 hours, with amounts of 510.30 mg/L, 232,70 mg/L and 544.316 mg/L respectively. However in the case where malic and tartaric acids were used as leaching agents there was a fluctuation of Fe concentration from the initial contact time. These fluctuations of metal concentration maybe attributed to time consuming reactions which lead to metals hydrolysis and precipitation process. Ca shows variability in leached concentrations with time showing that this metal may continue to leach for a long period of time, the similar trend with variability of metals has been reported by Kundu et al [1]. Citric acid and oxalic acid show high leaching efficiency of Ca than other organic acids, leaching of Ca from S2 showed maximum concentrations of 15 mg/L, and 11.66 mg/L using oxalic and citric acid respectively and 16.88 mg/L and 15.04 mg/L from S13 using oxalic acid and citric acid respectively. This might be due to the fact that organic acids such as citric and oxalic acids which form stable complexes with metals have a greater potential to mobilize them from the soil than those which do not [2].

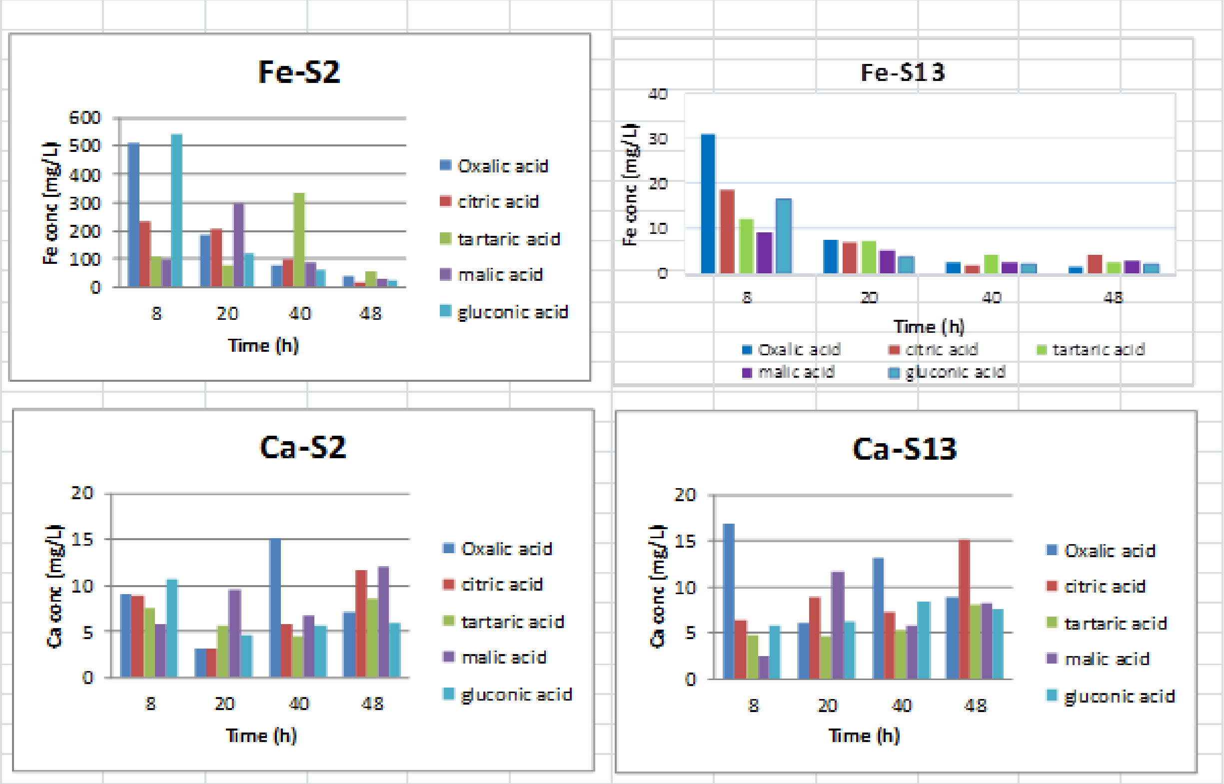


Fig. 1 Effect of time on release of Ca and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic acid.

Effect of pH

Figure 2 represents the results of the leaching behaviour of Fe and Ca at various pHs 3.5, 4.5, 5.5 and 6.5. From the figure, it can be observed that the leachability of all metals depends on its pH and the concentration. Leachates contain higher metal concentrations at lower pH for samples taken on the top of the tailing dump (S2). As shown at pH 3.5, high concentration (213.77 mg/L) of Fe is released while a decrease is recorded at pH 5.5 and 6.5 where the concentrations 173.11 mg/L and 26.06 mg/L are obtained respectively. A decrease in concentration from 11.69 mg/L, 8.04 mg/L to 5.83 mg/L is observed at pH 3.5, 4.5 and 5.5 respectively. The higher the concentration, the higher is the mobility of metals. The mobility of metals is high under acidic conditions (low pH), according to Fan et al. [11], the leaching of metals in such trend is due to the acidic attack. Dissolution of metals from sample collected at the bottom of the dump (S13) also revealed similar trend while using oxalic acid as the leaching agent; it was observed that the concentration of metals in the leachate decreased from pH 3.5 to pH 6.5. The concentrations decreased from 33.71 mg/L, 18.63 mg/L, 16.64 mg/L and 10.36 mg/L at pH 3.5, 4.5, 5.5 and 6.5 respectively. While using citric acid the amounts of Fe decreased from 14.99 mg/L, 14.17 mg/L, and 13.30mg/L to 9.88 mg/L under the same conditions. The removal of Ca by oxalic acid has shown a decreasing trend with increasing pH from 3.5 to 6.5 for both S2 and S13, however at pH 5.5 there is a fluctuation which has taken place. According to Guo et al [12], the fluctuations in concentrations should be ascribed to hydrolysis and precipitation. The Ca concentrations in the leachates of samples S2 and S13 were as follows; 9.77, 7.0 and 2.83 mg/L for pH 3.5, 4.5 and 6.5 respectively and 4.66 mg/L, 0.63 mg/L and 0.11 mg/L for pH 3.5, 4.5 and 6.5 while using oxalic acids as leaching agent. The pattern of Ca mobilization from tailing samples by citric acid is depicted in Figure 2, and the corresponding concentrations in the leachates are as follows: 9.34 mg/L, 4.41 mg/L, 4.35 mg/L and 2.72 mg/L for S2 and 9.14 mg/L, 6.68 mg/L, 4.25 mg/L and 1.40 mg/L for S13 at pH 3.5, 4.4, 5.5 and 6.5 respectively. Higher amounts of Fe and Ca are removed by citric acid in acidic medium (low pH) than at high pH. The higher the leached amounts found at low pH, the higher is the mobility. High concentrations of Fe were removed from the S2 samples than from the S13 samples, but the amount of Ca released from S2 was almost the same as the one released from the S13. This might be because of the high oxidation of Fe at the top of tailing dump than at the bottom of the dump. The mobility of Fe is higher than that of the Ca, this might be due to the fact that Fe form stable complexes with organic acids and that cause it to have higher mobility [13].

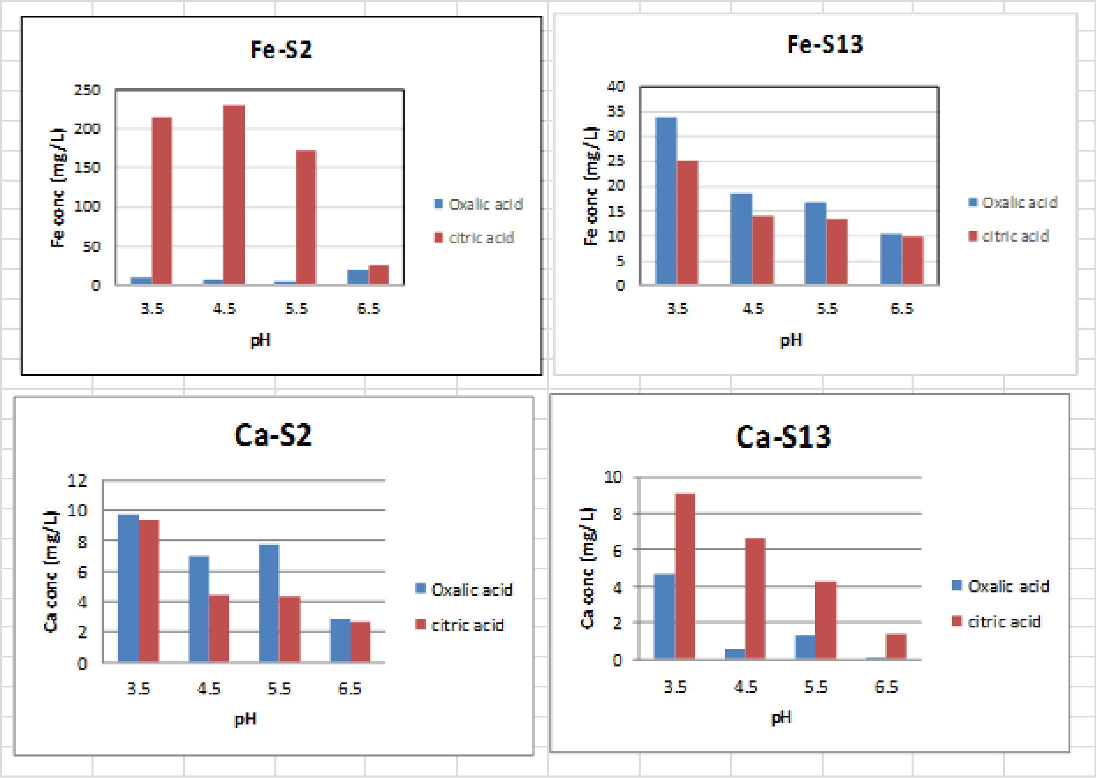
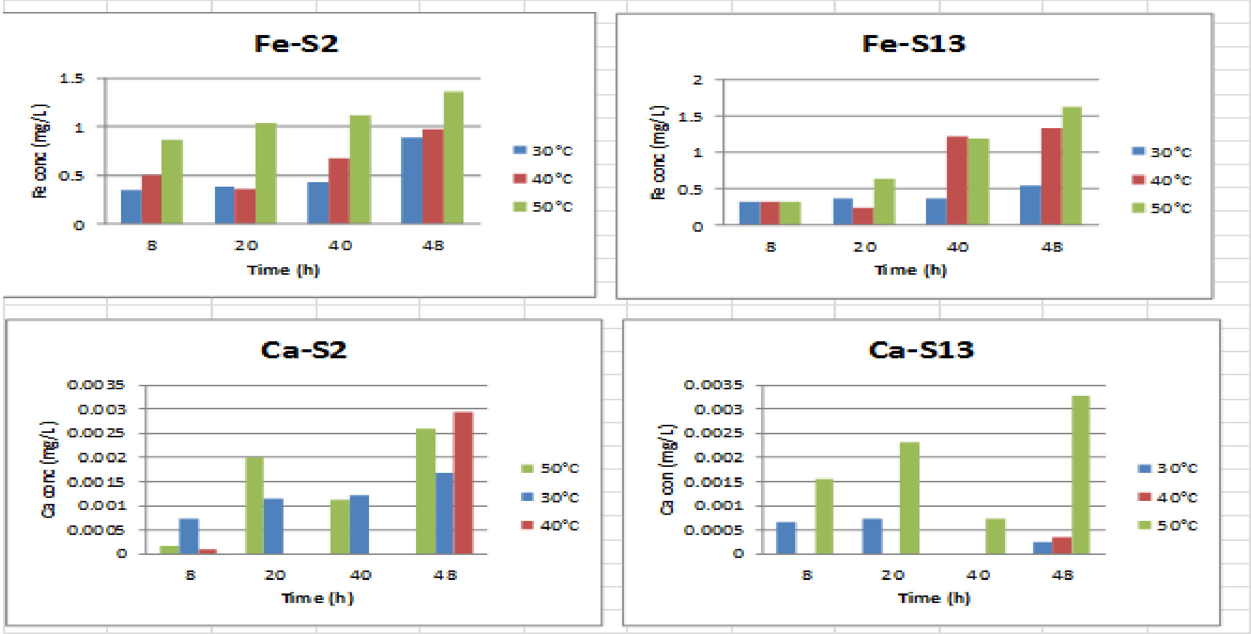


Fig. 2 Effect of pH on release of Ca and Fe from the top (S2) and bottom (S13) of tailing dump at 3mM oxalic acid and 48 hours contact time

Effect of temperature

The effect of temperature on metals mobilization properties is shown in Figure 3. As shown in the Figure, the mobility of Ca and Fe examined depends on the temperature and contact time. It is clear from the graphs that Fe and Ca exhibited the increasing trend of concentration with leaching time. The mobility of Fe was highly dependent of temperatures. The leaching with oxalic and citric acid revealed high mobility of Fe at temperature 50°C than at 30°C and 40°C for both S2 and S13. The leaching of Ca with oxalic and citric acid showed consistent increasing trend with leaching time than that of the low temperatures. A decrease of Ca release was observed at 30°C for S2 and S13 while leaching with citric acid and S13 only while leaching with oxalic acid, this might be due to the fact that organic acids can decompose especially when leaching hard dissolving compounds [14]. A decrease of metal concentrations during leaching with citric acid is a trend that was also observed by Habbache et al [14]. Fe was removed in high concentration than Ca, this might be due to the fact that Fe oxidizes better than Ca, which was confirmed by the XRF results. Fe is mobilized highly than the Ca, this might be due to the fact that organic acids form stable complexes with Fe according to Kim et al [15], organic compounds such as oxalic and citric acids form stable complexes with metals and have greater potential to mobilize metals from soil than those which do not. Gadd [13], have established that Al forms oxalate complexes with oxalic acid.



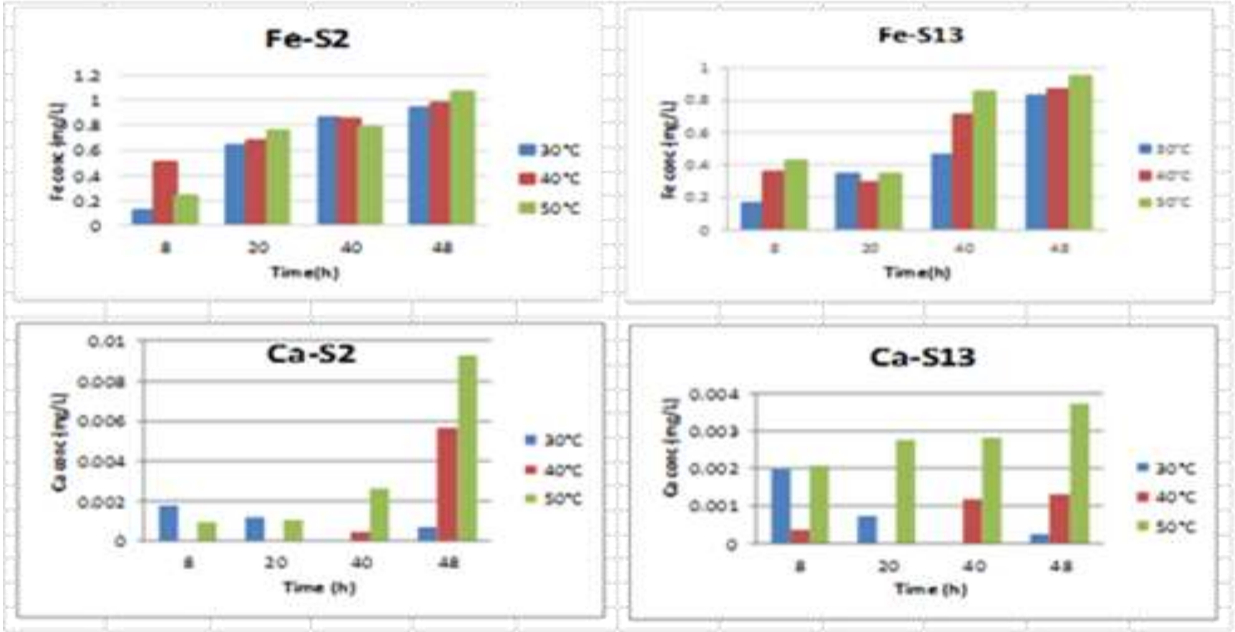


Fig. 3 Effect of temperature on release of Ca and Fe from top (S2) and bottom (S13) of tailing dump at 3mM (a). oxalic (b). citric acid and 48 hours contact time

CONCLUSION

The effect of organic acids on the mobility of metals from the tailings was studied. The mine tailings of Krugersdorp mainly contained Fe and Ca among others. The XRD results have shown the mineralogical composition of selected sampling sites S2 and S13, the Sillimanate and the catena-sillicate were the major minerals and contents of the mine tailings. The mobility of metals was promoted by the low pH and high temperature. For temperature effect, the metals were highly released at the late stages of leaching and at high temperature. Oxalic and Citric acid were found to be the most efficient leaching agents for the removal of Fe and Ca. The mobility of Fe in the tailings were higher than that of the Ca, this is due to the fact that Fe form stable complexes with organic acids which cause it to mobilize highly.

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The corresponding author is currently an Associate Professor in the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom). He is an NRF rated researcher who has published journal articles, book chapters and book.

Prof Elvis Fosso-Kankeu has been the recipient of several merit awards